



Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast



Hendrik Wolschke^{a, b, *}, Roxana Sühling^b, Wenying Mi^a, Axel Möller^c, Zhiyong Xie^a, Ralf Ebinghaus^a

^a Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, 21502 Geesthacht, Germany

^b Leuphana University Lüneburg, Institute of Sustainable and Environmental Chemistry, 21335 Lüneburg, Germany

^c GBA Gesellschaft für Bioanalytik mbH, 21073 Hamburg, Germany

HIGHLIGHTS

- Yearlong investigations of OPEs in the atmosphere.
- Gas/particle phase partitioning of OPEs.
- Advantage of GC-MS/MS method.

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ABSTRACT

This study reports the occurrence and distribution of organophosphorus esters (OPEs), used as flame retardants and plasticizer, in the marine atmosphere of the German Coast. From August 2011 to October 2012, 58 high volume air samples (gas/particle phase separately) were collected at the German North Sea coast town Büsum. With the use of a GC-MS/MS System for instrumental analysis, detection limits for OPEs in air samples could be significantly improved compared to the previously used single GC-MS method. The concentration (gas + particle phase) of total OPEs was on average 5 pg/m³, with eight of the nine investigated compounds detectable in over 50% of the samples. A focus of this investigation concerned the partitioning of OPEs between the particle and the gas phase. The observed partitioning of OPEs in this study was distinguished from previous studies. While previous studies reported OPEs exclusively in the particle phase, a significant part of the sum OPE concentration (55%) was detected in the gas phase. The contribution of the gas phase even reached up to as high as 88% for individual compounds such as tri-iso-butyl phosphate.

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1. Introduction

Organophosphorus compounds (OPEs) are high production volume industrial chemicals which are widely used as plasticizers and flame retardants in various household and industrial products (Marklund et al., 2003). Varying alkyl- and aryl-ester groups, some of them halogenated, lead to a large variation in the physico-chemical properties. Octanol-water (KOW) and air-water (KAW) partitioning coefficients range from log K_{OW} of −1 (trimethyl phosphate) to 11 (Tetrakis(2,6-dimethylphenyl)-*m*-phenylene

biphosphate) and log K_{AW} of −12 (Tetrakis(2-chloroethyl)dichloroisopentyldiphosphate) to −3 (Triisobutyl phosphate) (Zhang et al., 2016). Halogenated OPEs are mainly used as flame retardant, whereas non-halogenated OPEs are predominantly used as plasticizers and for other applications (Marklund et al., 2003). In the last decades OPEs have already been extensively used, yet they have recently, additionally, been recommending as substitutes for the banned polybrominated diphenylethers (PBDE) (Shaw et al., 2010). An increase in the OPE production and emission can therefore be expected and has started to become apparent. Even though first reports of OPEs in the environment date back to the 1970s environmental research and monitoring has only recently started focusing on these compounds (Reemtsma et al., 2008). Due to their long term use and recent increase of environmental relevance OPEs

* Corresponding author. Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, 21502 Geesthacht, Germany.

E-mail address: hendrik.wolschke@hzg.de (H. Wolschke).

are often referred to as “re-emerging” compounds (Reemtsma et al., 2008). OPEs are mostly used additively, which means that they are not chemically bound to the polymers they are used in, but merely blended into the product. Therefore, they have a high potential to leach out from the material by volatilization, abrasion and dissolution and enter the environment (Rodríguez et al., 2006).

Since the start of the newly increased scientific interest in OPEs, numerous studies have reported OPEs in indoor air (Björklund et al., 2004; Chung and Ding, 2009; Fromme et al., 2014), human blood, house dust (Fromme et al., 2014; Takeuchi et al., 2014), river water (Bollmann et al., 2012; Wang et al., 2015; Wolschke et al., 2015) and sediments (Chung and Ding, 2009), the great lakes (Venier et al., 2014), the marine water phase (Bollmann et al., 2012), as well as fish and biota (Campono et al., 2010; Sundkvist et al., 2010). However, studies reporting OPEs in ambient air are still limited. The few respective studies reported OPEs in in the atmosphere of the great lakes (up to 2.1 ng/m³) (Salamova et al., 2014b), over the North Sea (Möller et al., 2011) and in the Arctic (Salamova et al., 2014a). As early as in 1994, OPEs were reported in aerosols from Antarctica with up to 1 ng/m³, indicating a potential for long range transport. They were, furthermore, reported in Finnish air from a remote sampling site with up to 13 ng/m³ (Marklund et al., 2005), in air masses from Longyearbyen, Svalbard at 1.45 ng/L and in the water phase of closed volcanic lakes in central Italy (up to 951 ng/L) (Bacaloni et al., 2008). Möller et al. (2011) reported data on OPE concentrations in airborne particles along transects in the Pacific and Indian Ocean to the Arctic and South Pacific Ocean with OPE concentrations up to 3 ng/m³ in these remote marine areas.

In this study we present the results of continuous weekly sampling over one year in 2011–2012. Samples were collected over one week each at the sea side village Büsum at the shore of the North Sea. The occurrence of 9 OPEs was investigated separately for gas and particle phase. With this study we hope to contribute to the understanding of the complex problem of OPEs in the atmospheric environment and provide new insights into their environmental fate and behavior.

2. Material methods

2.1. Air sampling

Sampling was conducted weekly from August 3, 2011 to October 2, 2012 at the seaside village Büsum (54.13°N, 8.88°E), Germany (Fig. S1). A total of 58 air samples (about 2800 m³ over 7 day periods) were collected using a high-volume air sampler. A glass fiber filter (GFF, pore size: 0.7 µm) and a self-packed polyurethane foam (PUF)/XAD-2 cartridge (PUF: φ5.0 cm × 2.5 cm; 35 g XAD-2, particle size: 0.3–1.0 mm) were employed simultaneously to collect particle and gas phase separately. Field blanks of GFFs and PUF/XAD-2 cartridge were collected by exposing them for 1 min at the sampling site and subsequently treating them in the same way as real samples. Both PUF/XAD-2 cartridge and filters were stored at –20 °C in darkness until analysis. Detailed information on the sampling dates and air volume and are presented in Table S2.

2.2. Sample preparation and analysis

The presented method was refined from the method presented in Möller et al. (2011). Prior to extraction, PUF/XAD-2 cartridge and GFFs were spiked with 20 ng of mass-labeled surrogate standards ([d12]-TCEP, [d27]-TnBP, [d15]-TPhP). PUF/XAD-2 was extracted with a modified Soxhlet extractor for 16 h using dichloromethane (DCM). Particle samples (GFF) were extracted using a standard Soxhlet extractor using DCM for 16 h. Extracts were concentrated to approximately 2 mL using hexane as keeper and passed over 3 g

Na₂SO₄ to remove residual water. For clean-up 2.5 g 10% water deactivated silica gel columns were used. Two fractions were eluted: F1 for non-polar compounds, using 15 mL of hexane and F2 for semi-polar compounds, using 20 mL of acetone/DCM (1:1 v/v). The F2 fraction contained the OPEs and was used for instrumental analysis. Both fractions were concentrated to 150 µL under a gentle stream of nitrogen and 500 pg of 13C-labeled PCB141 as injection standard were added prior to analysis.

2.3. Instrumental analysis

Analysis was performed on an Agilent 7010 gas chromatograph-tandem mass spectrometer (GC-MS/MS), fitted with a PTV injector in pulsed split-less mode. The initial temperature of the injector was held at 60 °C for 0.1 min and then increased at 500 °C min to 300 °C. The sample injection volume was 1 µL. Helium was as carrier gas at a flow of 1.3 mL min⁻¹. The GC was equipped with an HP-5MS column (30 m 0.25 mm i.d. 0.25 mm film thickness, J&W Scientific). The temperature program started at 40 °C held for 4 min, afterward increased by 5 °C min⁻¹ to 170 °C, held for 5 min, 10 °C min⁻¹ to 230 °C, held for 5 min, 5 °C min⁻¹ to 250 °C and finally 10 °C min⁻¹ to 300 °C. The MS transfer line and the ion source (electron impact chemical ionization, EI) were held at 280 °C and 230 °C, respectively. The MS was operated in multiple reactions monitoring (MRM) mode. Details on monitored mass transitions for the detection of OPEs and surrogates are presented in Table S3. Samples were analyzed for the following 9 OPEs: Tris(2-chloroethyl) phosphate (TCEP), Tris(dichloroisopropyl) phosphate (TDCP), Tris(1-chloro-2-propyl)phosphate (TCPP mix of isomers), tri-isobutyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP), triphenyl phosphate (TPhP), Tris(2-butoxyethyl) phosphate (TBEP), tri(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCrP, mix of isomers). [d15]-Triphenylphosphate ([d15]-TPhP), [d27]-Tri-*n*-butylphosphate ([d27]-TnBP), [d12]-Tris(2-chloroethyl) phosphate ([d12]-TCEP) were used as surrogate standards. Information on CAS-No., producers, and purities of the used OPE standards are listed in Table S4 in the supplement material.

2.4. QA/QC

Since OPEs are widely used and therefore are also likely to be present in various lab equipment, the use of any plastic and rubber material was avoided to minimize possible contamination of the samples during sampling, storage, transport, and extraction. The sampling equipment used to trap airborne particles was exclusively made of stainless steel. Before use, GFFs were baked at 450 °C for 12 h and wrapped in aluminum foil prior and after use. Glass cartridges were extracted with acetone and DCM by Soxhlet before use. All used glass ware was baked at 250 °C for 12 h and rinsed with acetone. Silica gel was Soxhlet extracted with DCM for 12 h and baked at 450 °C for 12 h prior to use. 10 field blanks were taken during sampling and treated similar to the real samples, but with only 1 m³ air being pumped through the collecting system. TiBP, TnBP, TEHP, TCEP, TCPP, TDCPP, TPhP, TEHP and TCP were detected in the blanks. Absolute blank values ranged from 50 ± 9 pg (TCP) to 814 ± 330 pg (TECP) and were similar between the blank replicates. Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation or, for those compounds with no detected blanks, from the instrumental detection limits at signal-to-noise (S/N) ratios of three. Based on a nominal sampling volume of 2000 m⁻³, MDLs ranged from 0.1 pg m⁻³ (TDCPP) to 1 pg m⁻³ (TBEP). Note that values below the detection limits were determined based on absolute MDL values (in pg OPEs absolute) due to the variation of the sampling volume. The recoveries of the surrogate standards were 95 ± 34% [D27]-TnBP,

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